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Selective detection of individual gases and CO/H_2 mixture at low concentrations in air by single semiconductor metal oxide sensors working in dynamic temperature mode

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ABSTRACT

Highly selective detection of various individual gases (CO, H_2, CH_4, C_3H_8, NO, NO_2, H_2S, SO_2) at low concentrations (0.01–667 ppm) in air by a single SnO_2-based metal oxide sensor (MOX-sensor) is presented. The sensor operates in dynamic temperature mode combined with a number of adaptive signal processing algorithms. Artificial neural networks were proven to be more effective among the other adaptive algorithms implemented in this study. Identification of individual gases by a single sensor, averaged over all the gases and concentrations, resulted in only 13.2% false recognitions. Most of the failures were attributed to NO_2 detection in 0.01–0.1 ppm concentrations range.

The ability of a single sensor to identify gas mixtures in a complex background was tested on the example of CO + H_2 mixture in air, which simulates smoldering in the early stages of fire. The algorithm showed the ability to identify and quantify CO + H_2 mixture with less than 10% error rate, even in constant presence of background gas (NO_2 1.4 ppm). Chemical modification of SnO_2, increasing sensor response and sensitivity to individual components of the mixture, was proven to be beneficial for improvement of identification and quantification of gas mixture. Significant improvement in quantification accuracy (decrease in relative error from 7 to 2.5%) was achieved by utilizing a 3 sensor array in combination with an adaptive data processing algorithm, compared to the use of a single sensor alone. The prominent negative effect of humidity (Rh 30%, 25 °C) on the performance of adaptive algorithms, sensor signal processing, system selectivity, and gas mixture identification is demonstrated.

1. Introduction

Metal oxide (MOX) semiconductor gas sensors are promising components of modern instruments for express analysis of air chemical composition due to their high sensitivity, low cost, miniature size, ease of application, and low power consumption [1,2]. However, the main obstacle to their implementation is their high intrinsic cross sensitivity to a wide variety of gases and volatile organic compounds [3]. This restricts the range of applications for MOX-sensors. Many efforts have been made and approaches have been tested to improve the selectivity [4], which includes: application of semipermeable membranes [5,6]; modification of chemical composition, geometry and morphology of the metal oxide sensitive layer [7,8]; use of pre-concentration [9] or catalytic pre-treatment [10] of analyzed air. One of the promising approaches is the use of dynamic temperature mode for a MOX-sensor combined with a mathematical analysis of sensor response [11,12].

Benefits of using dynamic temperature mode for metal oxide resistive type gas sensors were postulated decades ago [13,14]. They are based on the temperature dependent nature of the gas sensing process by semiconductor metal oxides [3,15]. In the case of the most common semiconductor metal oxide, used as a sensitive element for gas sensors – nanocrystalline SnO_2–the basic principle is band bending caused by changes in concentration of chemisorbed oxygen on the surfaces of the semiconductor grains while interacting with gas molecules.

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The heterogeneous chemical interaction between gases and metal oxides has been extensively studied in the field of catalysis [16]. Such an interaction includes the stages of molecular adsorption with a consecutive chemical transformation and desorption of products [17,18]. Chemical transformation of the adsorbed molecules from the ambient air mainly leads to a complete or partial oxidation with a number of intermediates. The oxidation is achieved through a number of parallel processes on the material's surface, especially in the case of increasingly complex organic molecules [19,20].

Even the exposure to NO_2 gas results in a number of chemisorbed species on the SnO_2 surface, before being desorbed back in the atmosphere [21]. This means, that when sensing material is kept at constant working temperature, its response to a given gas is governed by a steady state equilibrium of the above mentioned chemical reactions occurring on the surface in a parallel manner [22]. Since the vast majority of gases and volatile compounds are reducers, then the response of such a sensor would lack selectivity. Rates of these processes greatly depend temperature [23]. Adsorption is favored by low surface temperature of a sensor, while chemical transformation and desorption of products is catalyzed by an increase of sensor working temperature. On the other hand, the semiconductor's electrical resistance drops with the temperature increase, which reduces the impact of surface chemical reactions on the material's conductance and, as a consequence, sensor response. Thus, for gas sensors, there is a certain optimum temperature, determined by the combination of metal oxide chemical and electrical properties, at which the response to a given gas is maximized [24]. This optimum sensor temperature may differ significantly for various gases, especially in the case of chemically modified sensor materials. Adjustment of optimum temperature may provide some considerable improvement of MOX-sensor response selectivity [25].

Cycling the sensor's operating temperature, instead, allows one to exploit the individual influence of each of the chemical processes occurring in parallel on the sensor's surface during the solid-gas interaction [26]. Either impulse temperature changes of sensing material or smooth temperature modulation leads to a transient chemical state of the semiconductor's surface at each point of the temperature cycle. For each particular temperature, any of the parallel chemical processes on the surface may be decisive for the material's resistance value [27,28].

Appropriate mathematical procedure is then required to analyze the shape of the sensor's response curve, measured during the temperature cycle, which bears characteristics unique for a given gas [29]. This approach allows one to identify and quantify individual gases and complex gas mixtures [30–32]. Another advantage of using temperature modulation is the ability to increase sensitivity towards a wide range of gases. The low temperature stage of each temperature cycle may be used to adsorb and accumulate i.e. concentrate measured gas on the surface of the sensor material [13,33].

The main issue then is to define properly the sensing element temperature cycle. Adjustable parameters for the cycle are: minimum and maximum temperature values; temperature increase and decrease rates; linear, sinusoidal or other type of temperature vs. time dependence; cycle length in accordance with the demands of analysis time limitations. These parameters are dependent on sensor design, porous sensing layer dimensions and thickness [34].

For the signal processing and pattern recognition, machine learning methods have been of great interest to the sensor community in the recent years, especially for the researchers working in the area of electronic noses and machine olfaction. These methods include: artificial neural networks, discriminant analysis [35], principal component analysis [36] etc. Application of such data processing algorithms implies building a multivariable statistical model, describing the structure of the data under consideration, and in most cases a frequency statistics [37] approach is utilized. Adjustment of variables in the model is being conducted through classical procedures of successive fitting of the model with the use of gradient descent algorithms [38], simulated annealing technique [39], ordinary least squares method and so on. This approach bears an implicit assumption that each data sample under investigation is representative and the appearance of different examples in it is equally possible. Moreover, in most of the algorithms (for example PCA, LDA etc.) the normal distribution of data is assumed, which does not happen in practice. This assumption is true for every data sample only when the law of large numbers is fulfilled, however in most practical cases the data samples under consideration are small [40]. Another important problem, frequently encountered in research papers, is the absence of testing procedures for the created adaptive models on the independent data sets [41,42]. Unfortunately, the expenses, associated with the obtaining of the data samples in the field of gases and gas mixtures detection, lead to working on small data samples, which does not allow one to perform rigorous statistical test with the degree of belief, for example, 5%. Nevertheless, researchers usually have initial considerations on the special features on the gas sensor performance and can demonstrate the sustainability of their work at least under the conditions of the given experiment [34]. However, in most cases the adaptive models (artificial neural networks for example) have far too many parameters, and this is the reason why overfitting of the models is usually observed and their error on the training data sets becomes zero [43]. At the same time, these models give inadequate response when new data samples are applied.

In the present work, the authors demonstrated the abilities of the gas detection system, which uses the machine learning algorithms. The fitting of the models is carried out in accordance to the frequency statistics approach with the use of big samples of data (more than 10 000 of examples for each subject in the training set) and securing the representativeness of the data samples set. The latter was achieved through equal number of examples of different analytes (gases and gas mixtures) and examples of the same analytes, obtained in different conditions (dry air and humid air). The quality of the created models has been tested with the use of data, obtained in the independent experiments, thus expelling the influence of local factors such as drift, specific for particular experiment, level of sensor degradation etc. It is noteworthy that all the described procedures of data handling are applicable to the new additional independent data samples and their connection with the model training set of data samples consists only of the scaling procedure.

2. Experimental

2.1. Sensor fabrication

All sensors were fabricated by using originally synthesized nanocrystalline SnO_2-based gas sensing semiconductor materials. Pure nanocrystalline as well as chemically modified SnO_2 was used in the study. On the basis of our previous research [7,25] PdO_x catalytic component and Fe_2O_3 oxide modifier were taken. The synthesis technique, based on sol-gel and impregnation procedures, was described in detail in previous works [25] and was reproduced in very detail in the present work. Briefly – the α-stannic acid gel was precipitated from an aqueous solution of $SnCl_4{\cdot}5H_2O$ by the addition of aqueous ammonia (to pH = 6.5–7.0) with continuous stirring at 0 °C. The precipitate was separated by centrifugation, thoroughly washed with distilled water to remove chloride ions, and dried at 100 °C for 1 day, and annealed in air at 500 °C for 24 h (SnO_2 sample). The modification of SnO_2 by Pd or Fe was